CHAPTER 7

Conclusion

Abstract

This chapter presents general and comprehensive conclusions of all the chapters.

This chapter deals with the general concluding remarks drawn from the previous chapters. The first chapter provides a brief introduction to the origin and advancement of research in the field of nonlinear optical property, two-photon absorption property and luminescent property. Theoretical formulations have also been outlined here to understand the structure property relationship for designing efficient materials in optical uses. It can be concluded that both organic and metal based systems possessing push-pull character are of enormous importance for use in optical devices due to their large first hyperpolarizability values. From the general discussion of the characterization of the luminescent materials, one can argue that singlet emitters can also take the advantage of singlet harvesting effect by gathering both triplet and singlet excitons and might be well suited for OLED applications as already established for triplet emitter materials.

The second chapter presents a brief theoretical framework of the measurements of hyperpolarizability (β) and two-photon absorption cross section (σ). Some of the methods *viz.,* Sum over states (SOS), Few-states model that are utilized in this thesis to quantify optical properties are explained in details.

Chapter three presents computational study of nonlinear optical properties of two synthesized systems, phenyl expanded and thienyl expanded thiophene fused nickel dithiolenes. Both the systems possess very low value of first hyperpolarizability. We systematically modify their structures by substituting neutral and zwitterionic donor-acceptor group at the aryl (phenyl and thienyl) ring to have high NLO response. After careful inspection of the HOMO-LUMO energies of all the six systems, we noticed that neutral donor-acceptor group marginally affects the HOMO energy level, whereas the LUMO is stabilized to some extent. Hence HOMO-LUMO energy gap (HLG) decrease. However LUMO energies are found to be significantly reduced for the zwitterionic complexes resulting large decrease in the HOMO-LUMO energy gap. Hence, HLG gradually decreases from neutral to ionic substituents for both sets of the designed systems. This observation has also been supported by the excitation energy calculations with TDDFT approach. From the calculated first hyperpolarizability values, it has been noted that the zwitterionic compounds possess very large values of β with low HLG. We find that by substituting ionic groups at the two ends of the Ni complex, the β values enhanced by at least 10-15 times than that of the molecules without any such substituent. By systematic analysis, a nice correlation between Δr index, TDM and β value have been observed. We anticipated that if synthesized, these molecules may prove to be useful in optical uses.

Chapter four provides computational study where we have considered the magnetic and optical properties of a few azulene based diradical systems. We have studied six diradical systems based on nitronyl nitroxide radical moiety and azulene as coupler. The magnetic property has been assessed through the magnetic exchange coupling and magnetic anisotropy. The calculated magnetic exchange coupling parameters J depict that among the six diradicals three are ferromagnetic, and three are antiferromagnetic. The magnetic exchange coupling constants have been corroborated through spin density alternation protocol. The spin density analyses of the three ferromagnetic diradicals depict an interesting alternation behavior in the azulene coupler. The junction carbon atoms of the two rings in azulene coupler always show similar spin density despite being neighbors. This behavior is a fascinating variation of the spin density alternation rule. The ability of the ferromagnetic diradicals as photosensitizer in photodynamic therapy is evaluated through the computation of the two-photon absorption cross-section. The integrative photodynamic therapy (IPDT) of tumors relies on the combined use of different factors that enhance the usefulness of IPDT.[237] The observed TPA cross-section values range in the reported limit of commonly used photosensitizing agents. Another dimension of the multi-property diradical system has also been explored in this work. The magnetic anisotropy of the ferromagnetic diradicals has been estimated through the zero-field splitting parameter D. A negative ZFS parameter suggests the tendency of the spin vector to orient along a specific Cartesian direction. All the three ferromagnetic diradicals show negative D values. Radical systems with negative ZFS parameters have been proved to be usable as MRI contrast agents.[188] It has long been shown that the larger the ZFS magnitude a_2, larger is the spin relaxation time and the better an MRICA is.[198] The ZFS magnitude a_2 is directly proportional to the ZFS parameter D. In the designed ferromagnetic diradicals, the ZFS parameters are found to be significantly high as for organic radical systems. The values are at least one order of magnitude higher compared to reported diradical systems usable as MRICA. Ferromagnetic systems are used as efficient probe in the magnetic hyperthermia, a popular treatment in oncology. These diradicals can also be sought for a lateral use as MRICA in magnetic resonance imaging, which is very often utilized for the detection of cancer. Treatment of interstitial tumors with PDT demands the delivery of photosensitizers to the precise location of tumor tissues for effective light irradiations. Thus a single agent that can be injected to the infected body to image tumors through MRI and simultaneously treat them by exposing to light through PDT is greatly welcomed as a proficient cancer treatment protocol. In summary we propose that if synthesized these diradical systems can promote the "see and treat" method[238] by proving themselves

efficient in multifarious therapeutic function such as magnetic hyperthermia, MRI contrast agents and photodynamic therapy applications.

In chapter five the photophysical property of an O_h Cr (III) complex is studied in the framework of density functional theory. Primary computational results of the absorption and emission wavelength obtained through TDDFT correspond well with the known phosphorescent behavior of the complex. In the later part, the axial ligands in the O_h $[Cr^{III}(NH_3)_6]^{3+}$ complex is replaced with comparatively weaker ligand so as to disrupt the O_h symmetry of the complex. The weaker ligand along the z-axis is expected to stabilize the d_{xz} and d_{yz} orbitals compared to the d_{xy} orbital and thus lifts the degeneracy of the erstwhile t_{2g} set of orbitals. This tetragonal distorted structure brings about electronic redistribution leading to the doublet state as illustrated in the Figure 3. Since, the difference in the strength of the axial and equatorial ligands is the key to further split the degenerate t_{2g} level, we logically replace the axial ligands of O_h $[Cr^{III}(NH_3)_6]^{3+}$ by I^-, Br^-, Cl^-, and F^- which are placed at different positions in the spectrochemical series with respect to NH_3. The propensity of the doublet state is high in the diiodo and dibromo complexes due to large difference in the strength of the I^- and Br^- ligands compared to NH_3. On the contrary, F^- and NH_3 are close in the spectrochemical series. Hence, the doublet state cannot easily be achieved due to equivalent strength of the axial and equatorial ligands. This fact of differing tendency for doublet state due to the variant strength of axial and equatorial ligands is supported by the low energy emission in the diiodo, dibromo complexes and high energy phosphorescence in the fluoro-substituted complex. The position of Cl^- lying between I^-, Br^- and F^- in the spectrochemical series matches well with the emission frequency of the chloro-substituted complex which is also in between the emission frequencies of iodo-, bromo-substituted complexes and fluoro-substituted complex. Thus, here we can see the relative position of the ligands in the spectrochemical series turns effective in tuning the emission frequency of phosphorescence. The most important finding of the present work is the blue-shift in the emission wave-length of $[Cr^{III}(NH_3)_4F_2]^+$. An emission wave length of 454 nm of this complex may offer significant insight for the rational designing of hitherto rare blue-emitting first row transition metal complexes, important for OLED applications.

Chapter six concludes with the observation that H-bond interaction stabilizes the electronic excited state in case of 2-amino pyridine resulting red-shift in the emission spectrum.